A STUDY OF THE CHEMILUMINESCENT REACTIONS OF SOME
ORGANOMETALLICS WITH ATOMIC OXYGEN

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ORGANOMETALLICS WITH ATOMIC OXYGEN

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INTRODUCTION

The chemiluminescent reactions of atomic oxygen with some hydrocarbons (formaldehyde, methyl alcohol, acetylene, ethylene, ethane, ethyl alcohol, benzene, etc.) were first studied by Harteck, et al. [1]* and Geib [2]. Geib and Vaidya [3] and Geib [4] reported the spectroscopic study of the above reactions. Gaydon [5] has summarized the previous studies related with the chemiluminescent reactions of atomic oxygen in so called atomic flames. The detailed studies of the chemiluminescent reactions of hydrocarbons [6], nitric oxide [7] and carbon monoxide [8] with atomic oxygen have been reported by this laboratory.

Similar extensive information regarding the gas phase chemiluminescent reactions of organometallic compounds with atomic oxygen is not available. However, some indications of their chemiluminescent reactions can be obtained from the diffusion flame study of tetraethyl lead, dimethyl zinc and dimethyl cadmium by Egerton, et al. [9]. Moreover, Harteck, et al. [10] have observed the chemiluminescence during the reactions of trimethyl aluminum, triethyl aluminum and triamthyl aluminum. They found that among the above mentioned organometallic compounds, the most intense chemiluminescence was observed during the reaction of trimethyl aluminum and atomic oxygen. All of the organometallic compounds studied by Harteck, et al. [10] contained the same metallic constituent, i.e., aluminum. We have recently completed the preliminary observations of the gas phase chemiluminous reactions of trimethyl aluminum, triethyl boron, trimethyl boron, trimethyl antimony and diethyl zinc with atomic oxygen. We have found that trimethyl aluminum is not the only organometallic compound which produces strong chemiluminescence with atomic oxygen, but boron and antimony compounds also produce a very strong chemiluminescence during the gas phase reactions with atomic oxygen.

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*Numbers in [ ] throughout text indicate reference numbers.

EXPERIMENTAL

A conventional fast flow system suitable for the study of gas phase re-
actions in the 1 mm pressure region was used for the present study. The ap-
paratus manifold is shown in schematic form in Figure 1. Atomic oxygen was
produced by a microwave discharge through about a 100:1 mixture of argon and
oxygen which provides a sufficient concentration of atomic oxygen in the pres-
ence of a small concentration of molecular oxygen. The flow tube dimensions
were such that the linear velocities of gases were of the order of 1000 cm/sec.
Therefore, the depletion of atomic oxygen due to recombination between the dis-
charge and the point of mixing was small. Except for trimethyl aluminum which
was obtained from Texas Alkyls, the other compounds were obtained from Alfa
Inorganics. Due to the pyrophoric and explosive nature of the organometallics,
a special handling and sampling procedure was necessary. The system utilized
for transferring the reactants is shown in Figure 2. It consists essentially
of a cross with stop cocks on the horizontal arms (one for pumping, the other
for flushing), a ground male joint on the lower arm (to which is fitted the
sample cell) and an open tubing on the upper arm for connection to a cylinder
of liquid organometallic.

The system is pumped and flushed with dry nitrogen before opening the
reactant cylinder. After several flushings the entire cross is left under a
sub atmospheric pressure of dry nitrogen and the cylinder is opened slightly.
The reactant liquid flows down into the sample cell where its vapor pressure
is lowered by a dry-ice acetone trap. The cylinder is closed and the entire
cross pumped and flushed again several times. Leaving the liquid under its
own vapor pressure the stop cock is closed and the cross once again pumped and
flushed. Under atmospheric nitrogen, the stop cock from the flushing side is
removed and air is allowed to diffuse into the system. The sample cell is re-
moved from the cross along with the dry-ice acetone trap and connected to the
reaction system.

The vapors of the organometallic compounds were admixed through a nozzle
in a 2 cm i.d. pyrex tube equipped with a quartz window. It was found that
after several minutes of reaction the nozzle was clogged due to the deposition
of metallic oxide. The reaction chamber was therefore modified by placing the
nozzle upstream in the organometallic vapor flow tube as shown in Figure 3.
With this arrangement, the nozzle also reduced the back diffusion of oxygen in
the organometallic vapor in the tube. In order to observe the chemiluminescence,
the appropriate relative flows of argon and oxygen were adjusted and the micro-
wave discharge was initiated. The usual afterglow was observed in the tube.
The organometallic vapor was then introduced. After a few minutes, it was ob-
served that the color of the afterglow started changing and was subsequently
replaced by the characteristic chemiluminescent glow. At this stage the rel-
ative flow rates of argon, oxygen and the organometallic vapors were adjusted
to maximize the intensity of chemiluminescent glow.

In order to ascertain the fact that the observed chemiluminescent glow
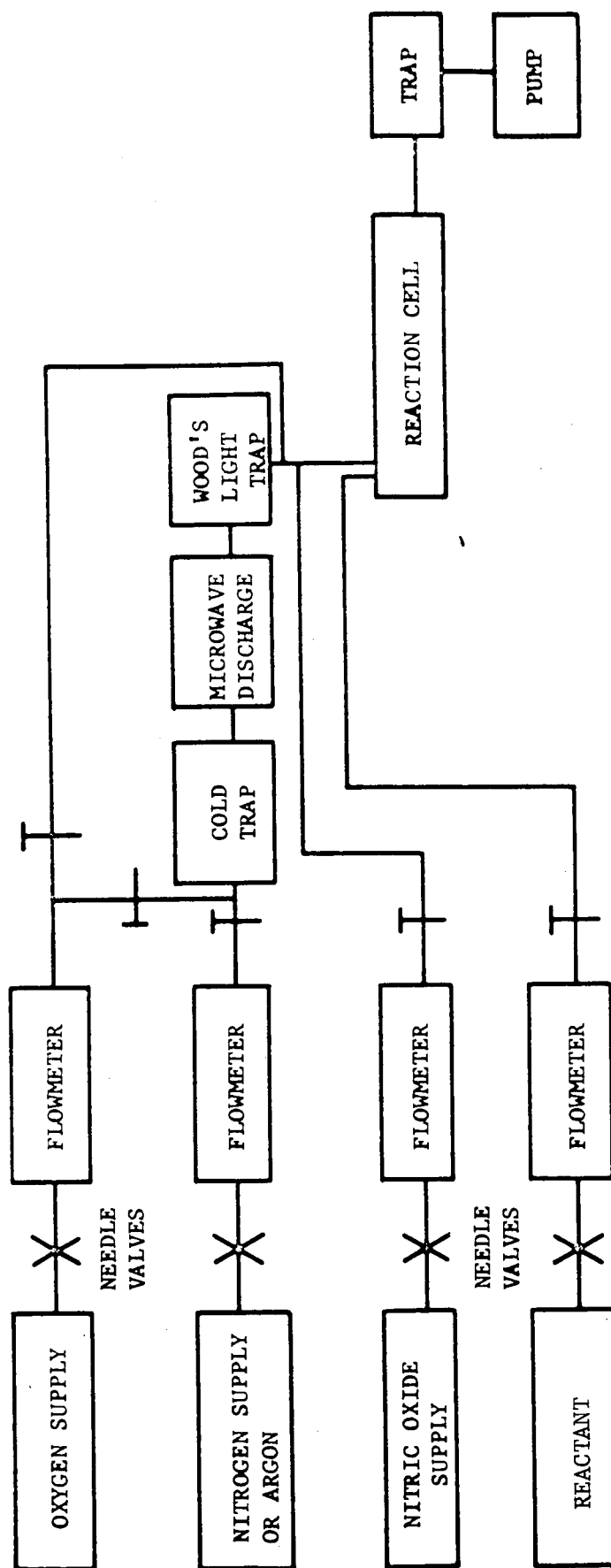was not due to the gas phase reaction between the organometallic vapor and

Figure 1. Block diagram of apparatus for observing chemiluminescence.
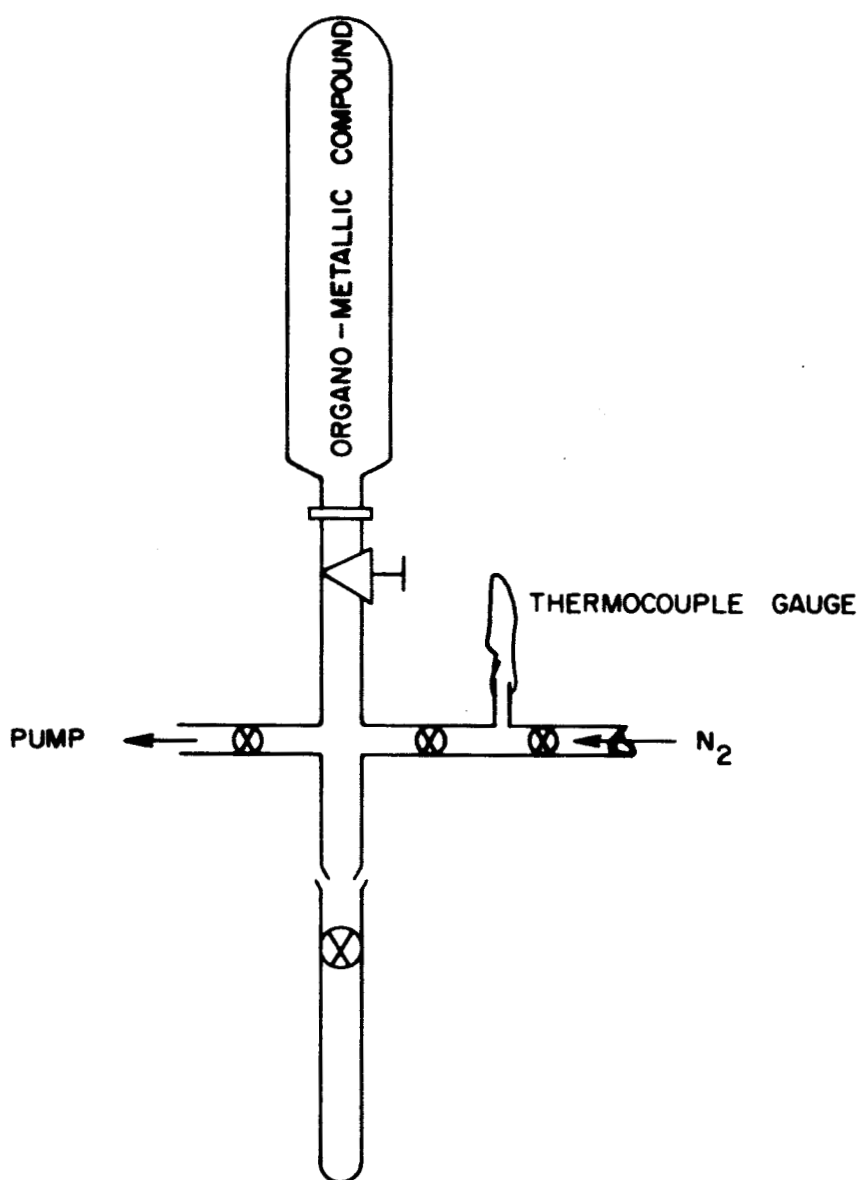
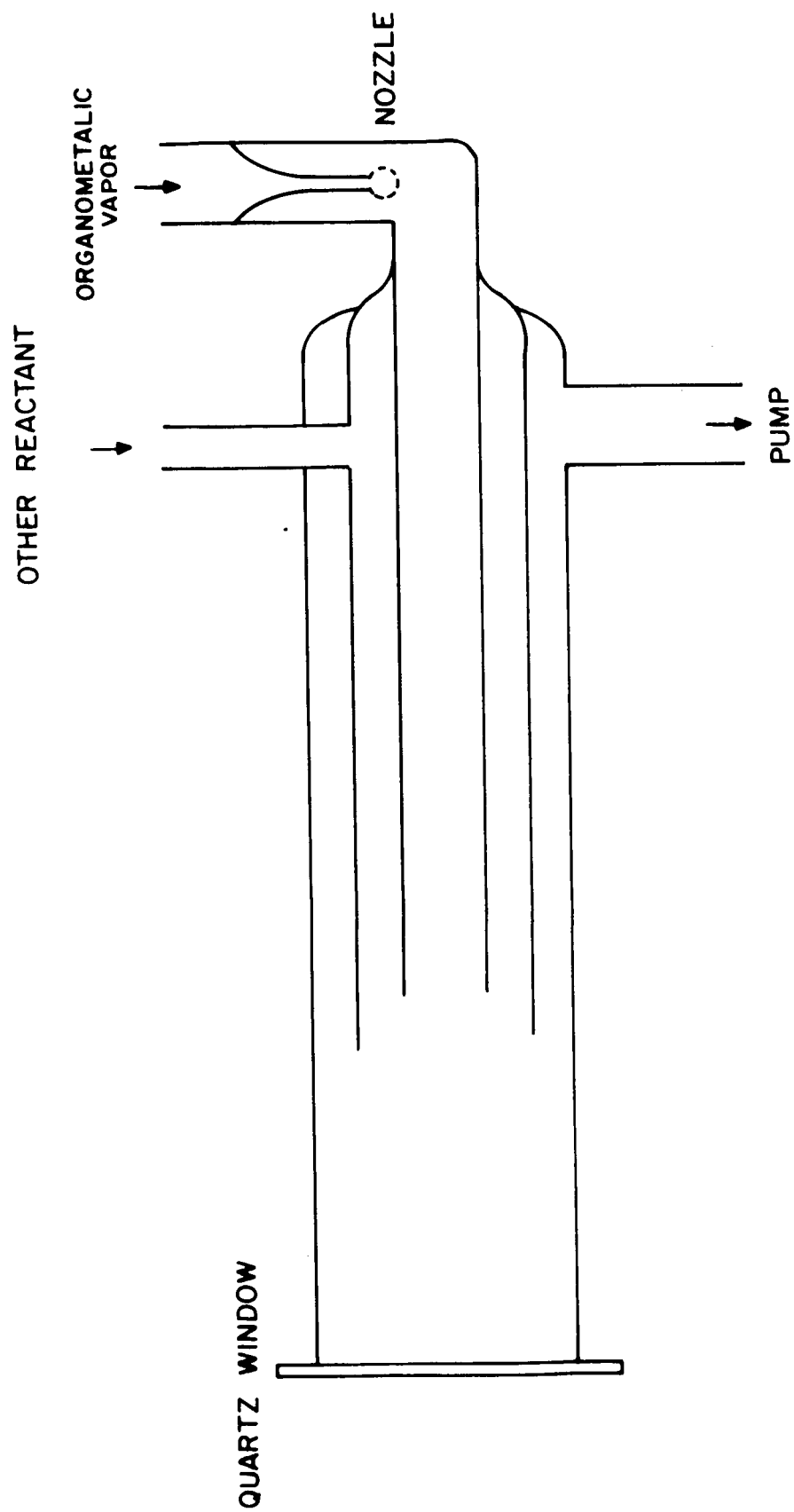Figure 2.   An arrangement for transferring organometallic compounds.

Figure 3. Reaction tube.

molecular oxygen, the discharge was shut off. It was found that the chemiluminescent glow reappeared as soon as the discharge was again initiated. The glow was also extinguished when the oxygen flow was stopped — indicating thereby that the discharged argon was not responsible for the observed chemiluminescence. It is therefore concluded from the above observations that the observed chemiluminescence was due to the gas phase reaction of atomic oxygen and organometallic vapor.

The spectra of the chemiluminescent glows were recorded with a Perkin Elmer (Model 99) monochromator equipped with a 600 lines/mm grating and an EMI 9558Q photomultiplier tube. In order to obtain the relative intensity of spectral features observed in the spectra, the spectral response of the recording system was calibrated with a standard light source (GE quartz iodine tungsten filament lamp, Model 6.6A/T4A/ICL-200W). The absolute irradiance of the lamp was obtained from Stair, et al. [11]. The corrected profiles of the recorded spectra are shown in Figures 4 through 7. The relative intensity of the spectra of different substances can be obtained from the gain factor of the amplifier used for the recording of the spectra and are shown in Figure 8.

The overall intensity of chemiluminescence produced during the reactions of organometallics with atomic oxygen was also studied at 100μ and 30μ pressures. For this purpose a 50 liter, 3 necked Pyrex flask was used (Figure 9). The gases flow into the cell through the two side arms of the flask. The center neck is connected to an oil booster pump backed by a Welsh mechanical pump which working together are capable of keeping the cell pressure at 10μ of Hg when the flow rates are up to 70 standard cc's/minute. The overall intensity was measured with an RCA 1P28 photomultiplier, which was placed in front of a small aperture sealed with a quartz window. The pressure within the cell was measured with a calibrated McLeod gauge. The photoelectric current was measured by an electrometer (Model VTE 1 of the Victoreen Instrument Co.).

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Figure 4. The corrected spectrum of the chemiluminescent reaction between trimethyl antimony and atomic oxygen.

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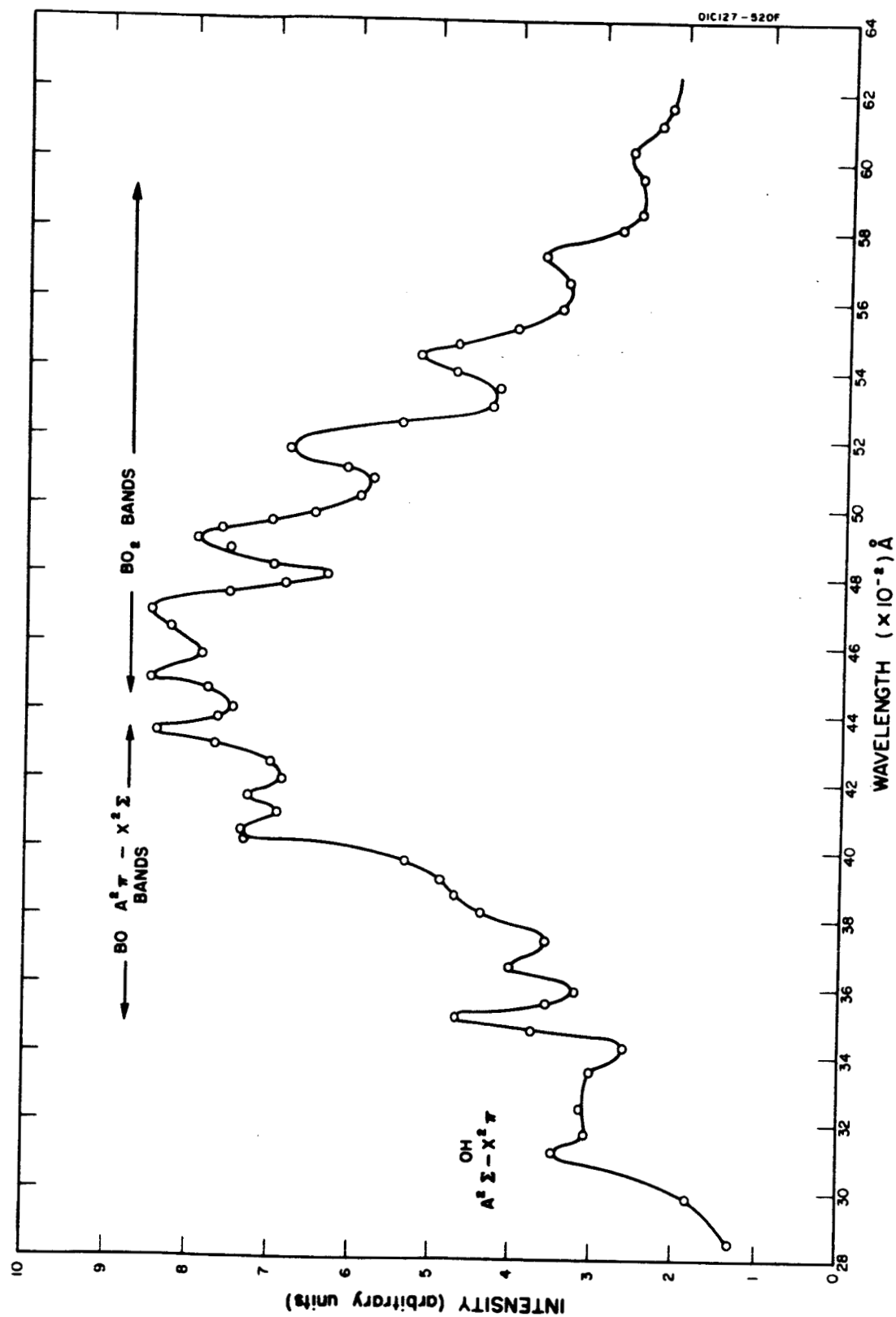
Figure 5. The corrected spectrum of the chemiluminescent reaction between triethyl boron and atomic oxygen. A similar spectrum is observed during the reaction of triethyl boron.

9
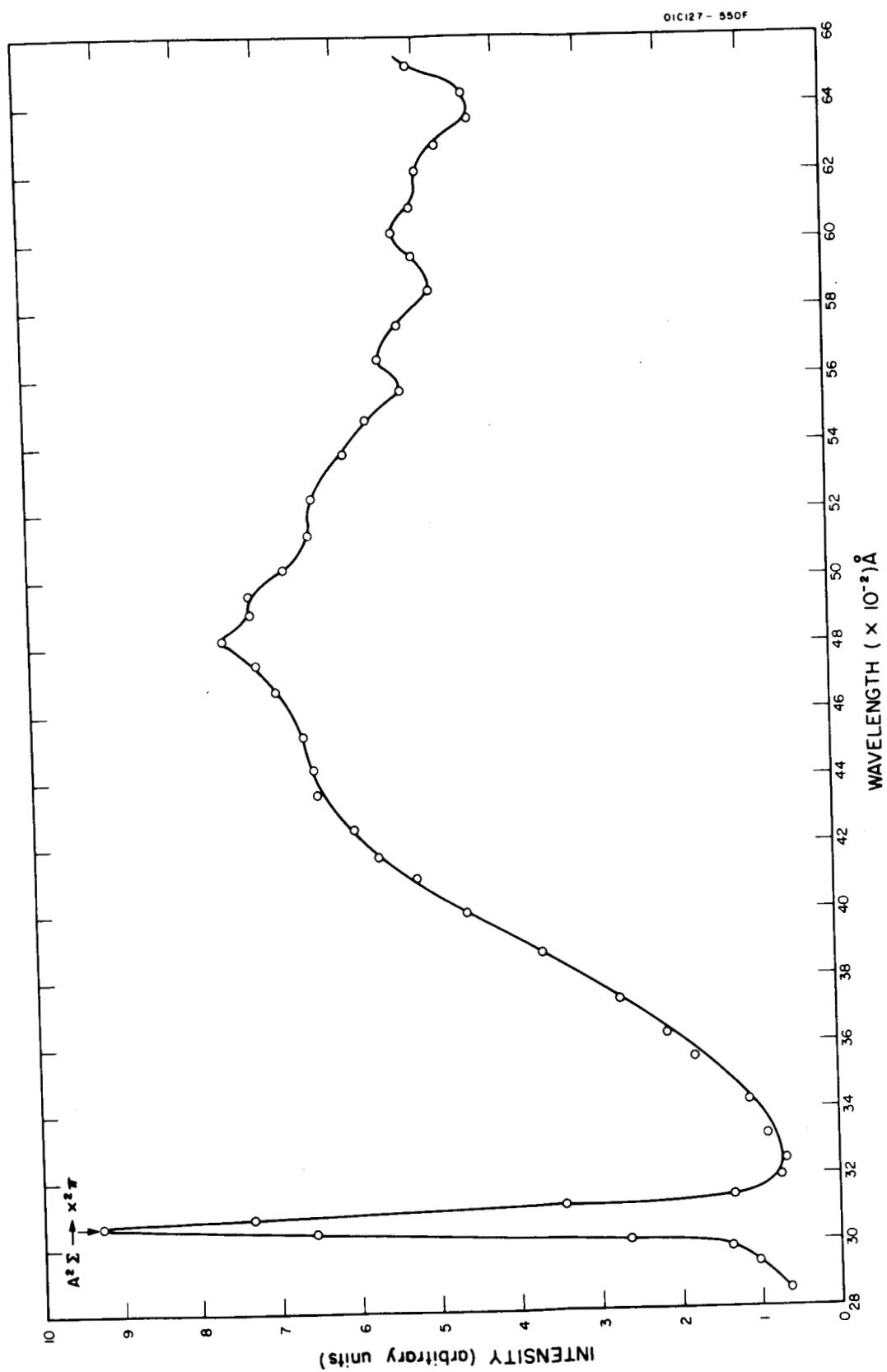
Figure 6. The corrected spectrum of the chemiluminescent reaction between trimethyl aluminum and atomic oxygen.

10
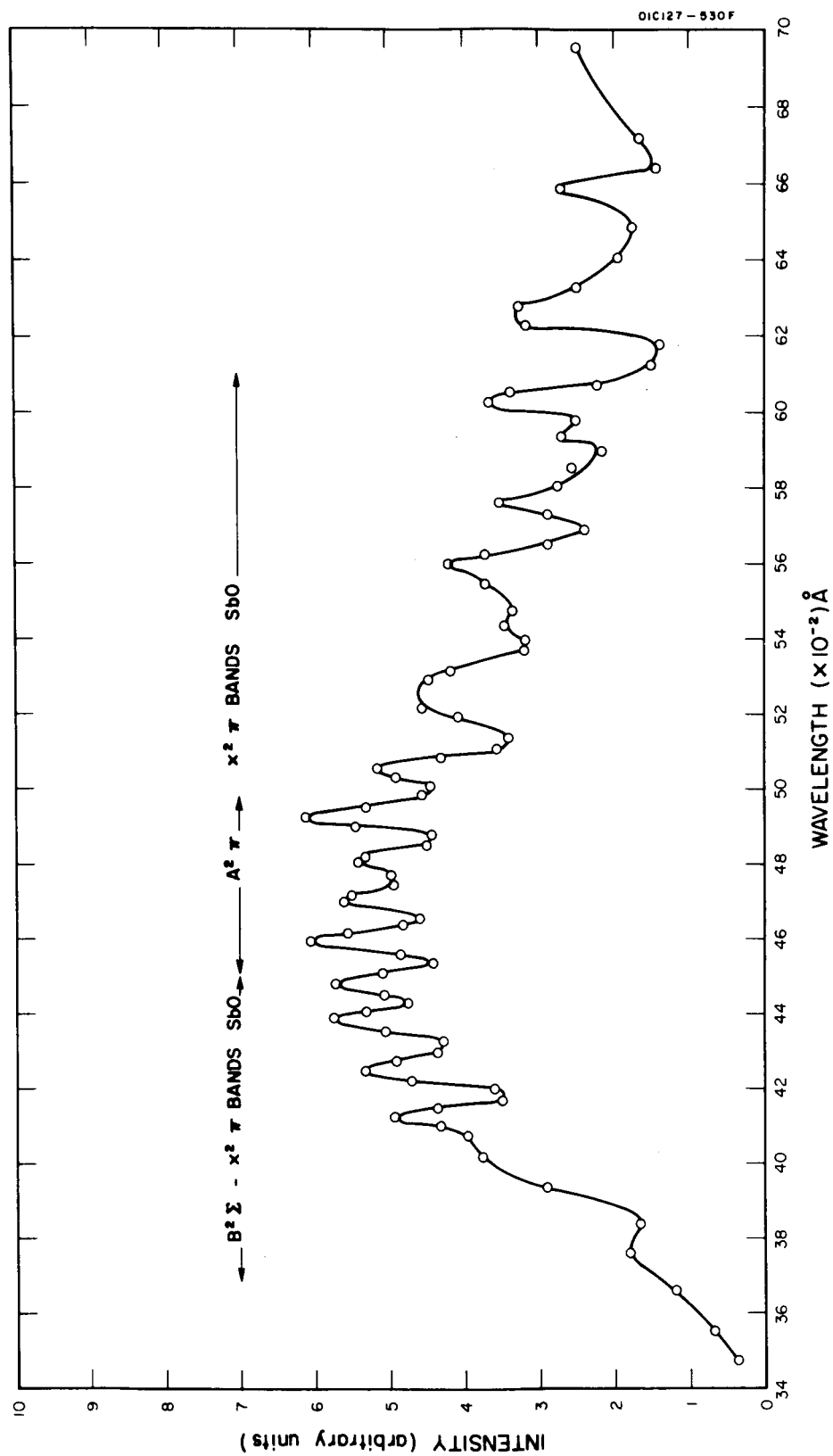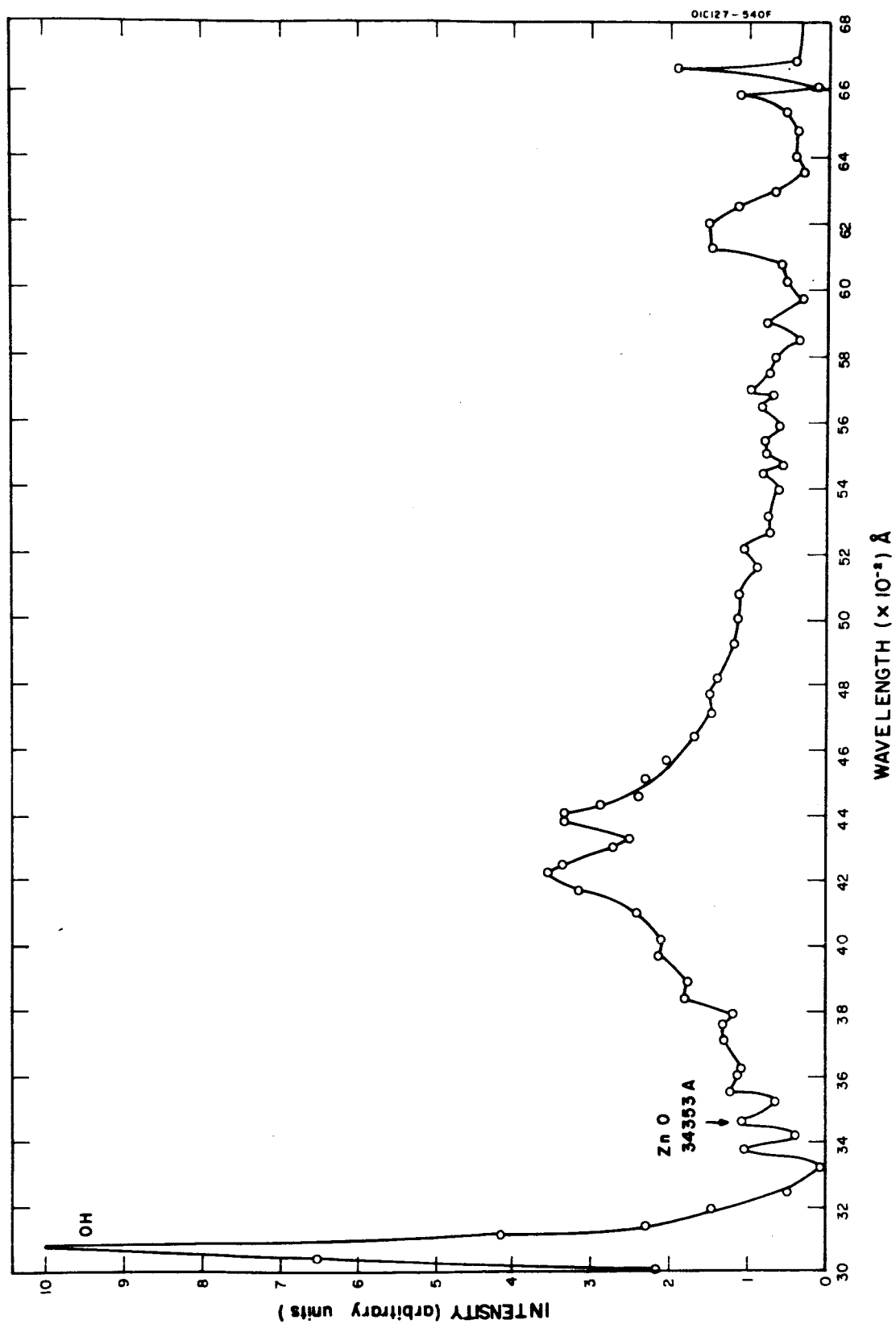
Figure 7. The corrected spectrum of the chemiluminescent reaction between diethyl
zinc and atomic oxygen.

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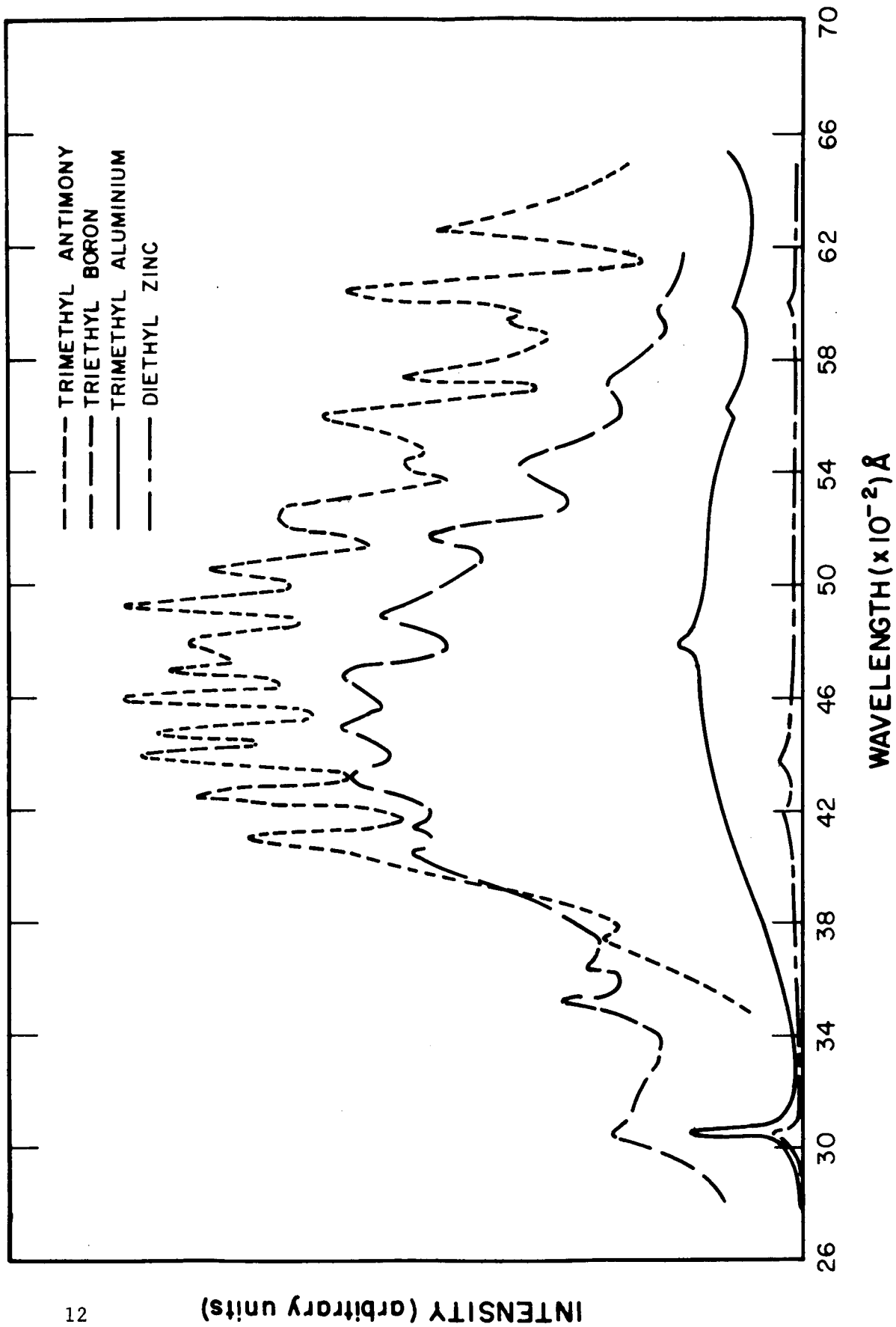
Figure 8. The spectra of the chemiluminous reactions of some organometallic compounds with atomic oxygen.

WAVELENGTH $(\times 10^{-2})$ Å

INTENSITY (arbitrary units)

TRIMETHYL ANTIMONY
TRIETHYL BORON
TRIMETHYL ALUMINIUM
DIETHYL ZINC

MAGNESIUM
OXIDE
LAYER

QUARTZ
WINDOW

(O, N OR O_3)

LEADS OF
HEATING WIRE

(NO OR NO_2)
(LIQUID VAPOR
REACTANTS)

McLEOD
GAUGE

TO
PUMPS

REACTANT GAS

Figure 9. Low pressure reaction chamber.

OBSERVATIONS AND DISCUSSION

The spectra of chemiluminescence produced during the reaction of trimethyl antimony and atomic oxygen consists mainly of A-X and B-X systems of SbO (Figure 4). The spectrum of SbO was first studied by Mukerjee [12] and SenGupta [13] in an arc between antimony and carbon electrodes. The above results were confirmed by Lakshman [14] in a heavy current discharge from a 2000 volt dc generator through Sb_2O_3 vapor. The preliminary identification of the spectral features recorded in the spectrum by the monochromator is given in Table I. The large discrepancy between the measured wavelength and that given by Pearse and Gaydon [15] is mainly due to the inaccuracy in the estimation of the wavelength of the recorded spectra. However, in addition to the previously observed bands, some unidentified bands are also observed which are listed in Table II. Some of the bands given in Table II may be identified with the bands of A → X and B → X systems of SbO given by SenGupta [13]. It may be noted that a number of new bands of the GeO molecule have been observed by Sharma and Padur [16] in the spectra excited by the chemiluminescent reaction of atomic oxygen and germane. This is due to the fact that the spectra excited by chemiluminescent reactions is comparatively free from the other interfering spectral features usually present in arc or discharge spectra. Moreover, the chemiluminescent reaction being a low temperature source, it produces a greater contrast between band head and the overlying structure of neighboring bands. Therefore, the chemiluminescent reactions of metallic compounds and atomic oxygen can be used for obtaining more information about the spectra of metallic oxides.

The spectra of the chemiluminescent reactions of both trimethyl boron and triethyl boron with atomic oxygen were similar and the spectrum is shown in Figure 5. The wavelengths of the observed spectral features together with identifications are given in Table III. It appears that the observed peaks above 4000Å may be due to BO_2 molecules as given by Mavrodineanu and Boiteux [17]. The bands below 4000Å at 3510Å, 3660Å and 3865Å can be due to 0-4, 0-3 and 0-2 bands of the BO α system. The other bands of the BO α system may also be present but it appears they are masked by strong BO_2 bands. One band at about 3100Å, which is presumably due to OH, has also been observed. The spectrum of the chemiluminescent reaction between triethyl boron and atomic oxygen was also recorded with a small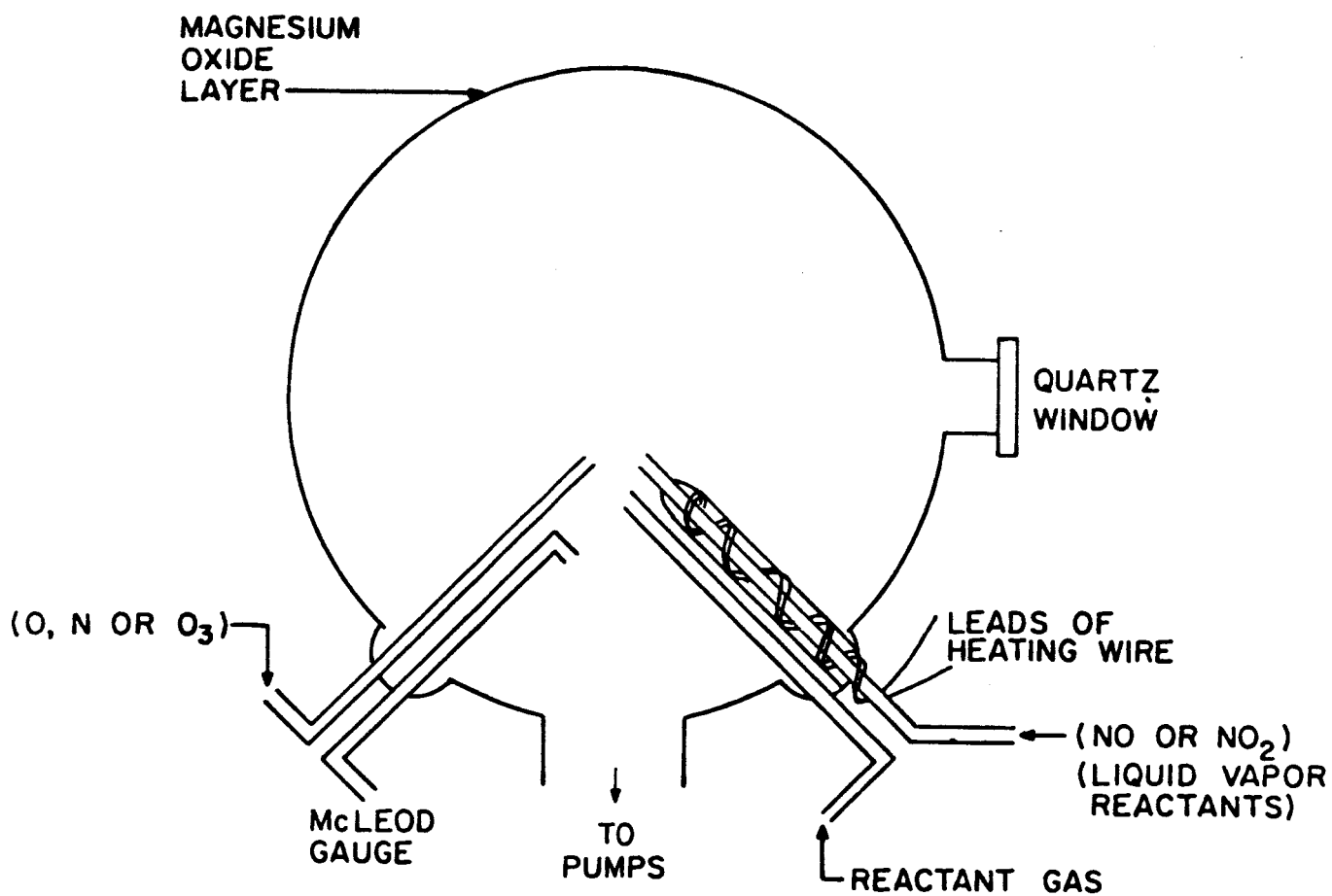 quartz spectrograph and is shown in Plate 1. The photographed spectrum shows an OH band at 3100Å and BO_2 bands about 4000Å only.

The spectrum (Figure 6) of the chemiluminescence produced during the reaction of trimethyl aluminum with atomic oxygen shows a continuous emission from about 3400Å to about 6600Å (the upper wavelength limit of the present detector). Harteck, et al. [10] have also obtained a similar spectrum. The presence of the OH band at about 3100Å is again indicated. The spectrum of the chemiluminescent reaction of trimethyl aluminum was also observed with a small quartz spectrograph (Plate 2) which also corroborates the above conclusions. The continuous spectrum observed during the chemiluminous reaction of trimethyl aluminum with atomic oxygen can be qualitatively compared with the spectra of chemiluminescence produced during the night-time release of trimethyl aluminum in the upper atmosphere [18].

TABLE I

THE SbO BANDS IDENTIFIED IN THE SPECTRUM OF THE CHEMILUMINESCENT
REACTION BETWEEN TRIMETHYL ANTIMONY AND ATOMIC OXYGEN

S. No.	Measured Wavelength (Recorded Spectrum)	Wavelength (Pearse and Gaydon [15])	Vibrational Transition v'	v"	Electronic Transition
1	3775	3774.0	0,	0	$B^2\Sigma \rightarrow X^2\Pi_{1/2}$
2	3880	3894.8	0,	1	$B^2\Sigma \rightarrow X^2\Pi_{1/2}$
3	3985	3987.9	3,	1	$B^2\Sigma \rightarrow X^2\Pi_{3/2}$
4	4070	4075.0	2,	1	$B^2\Sigma \rightarrow X^2\Pi_{3/2}$
5	4125	4130.2	0,	0	$B^2\Sigma \rightarrow X^2\Pi_{3/2}$
6	4265	4272.7	0,	1	$B^2\Sigma \rightarrow X^2\Pi_{3/2}$
7	4490	4504.7	3,	0	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
8	4550	4562.0	4,	1	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
9	4600	4617.2	2,	0	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
10	4665	4675.0	3,	1	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
11	4715	4736.8	1,	0	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
12	4790	4795.8	2,	1	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
13	4900	4926.2	1,	1	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
14	4980	4985.92	2,	2	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
15	5055	5064.0	0,	1	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
16	5130	5126.3	1,	2	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
17	5190	5189.9	2,	3	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
18	5280	5277.7	0,	2	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
19	5510	5505.6	0,	3	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
20	5765	5750.7	0,	4	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{1/2}$
		5757.9	1,	2	$A^2\Pi_{1/2} \rightarrow X^2\Pi_{3/2}$

TABLE II

UNIDENTIFIED BANDS IN THE SPECTRA OF CHEMILUMINESCENCE
PRODUCED DURING THE REACTION OF TRIMETHYL ANTIMONY
WITH ATOMIC OXYGEN

S. No.	Wavelength A
1	4290
2	4345
3	4370
4	4445
5	5435
6	5535
7	5595
8	5700
9	5865

TABLE III

THE IDENTIFICATION OF SPECTRUM OF CHEMILUMINESCENT REACTION
BETWEEN TRIETHYL BORON AND ATOMIC OXYGEN

S. No.	Wavelength A	Intensity Relative	Identification	
			Wavelength*	Emitter and Transit
1	3100	0.5	3021-3089	OH (0,0)
2	3510	1	3510-3526.8	BO α (4,0)
3	3660	2	3660.6-3679.1	BO α (3,0)
4	3865	3	3828.0-3848.7	BO α (2,0)
5	4050	5	4015.0-4037.4	BO α (1,0)
			4051-4090	BO_2 (B → X)
6	4150	6	4124-4145	BO α (2,1)
			4162.9-4168.9	BO_2 (A → X)
7	4340	7	4339.4-4365.9	BO α (1,1)
			4335.0-4349.0	BO_2 (A → X)
8	4510	10	4496.8-4506.1	BO_2 (A → X)
9	4690	10	4685.8-4694.8	BO_2 (A → X)
10	4900	8	4891.6-4917.0	BO_2 (A → X)
11	5160	6	5144.6-5183.5	BO_2 (A → X)
12	5430	4	5403.8-5470.1	BO_2 (A → X)
13	5725	2	5766.5-5790.7	BO_2 (A → X)

*The wavelength of BO bands are from Pearse and Gaydon [15] and those of BO_2 bands from Mavrodineanu and Boiteaux [17].

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THE SPECTRUM OF CHEMILUMINESCENCE PRODUCED DURING THE REACTION
OF TRIETHYL BORON WITH ATOMIC OXYGEN

BO_2 BANDS
$A \rightarrow X$

OH BAND (0,0)
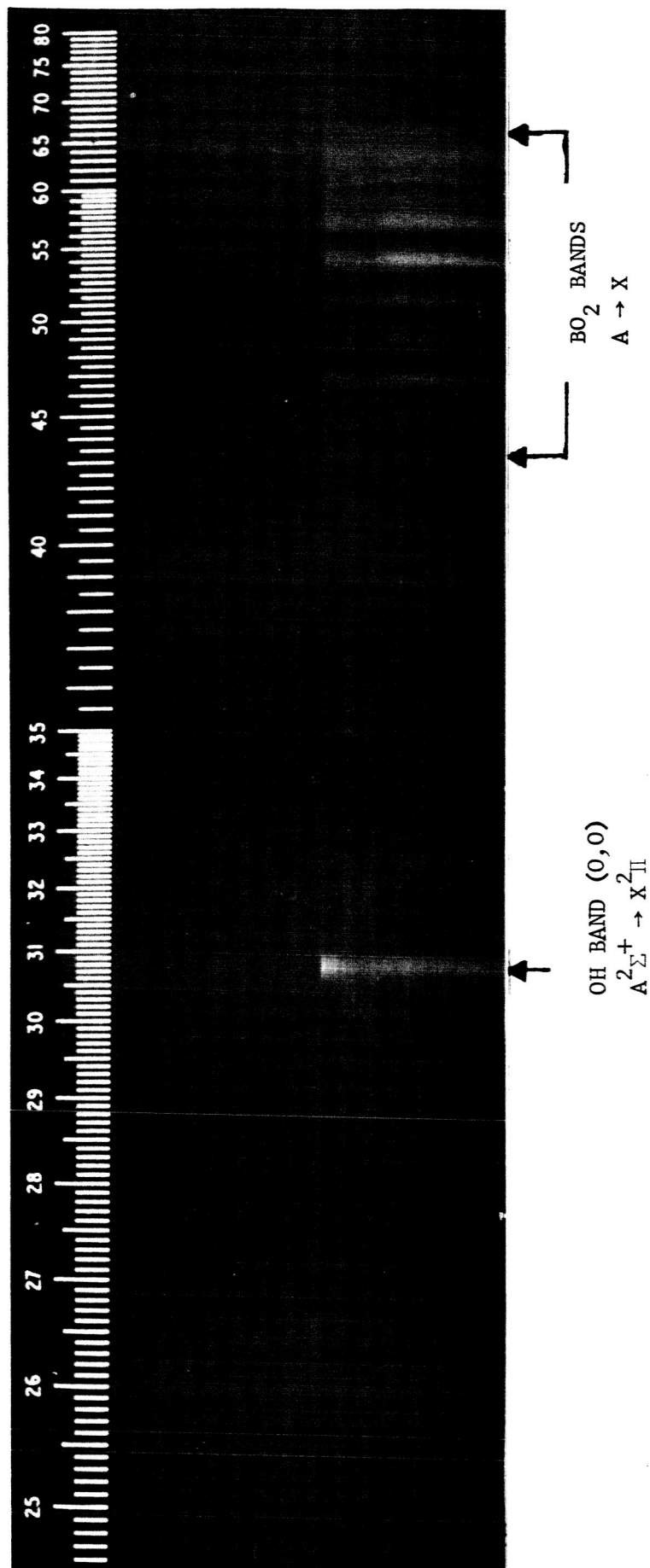$A^2\Sigma^+ \rightarrow X^2_{\Pi}$

PLATE 1- The spectrum photographed with a small quartz spectrograph.
The BO bands are not observable but were recorded with the
monochromator.

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THE SPECTRUM OF CHEMILUMINESCENCE PRODUCED DURING THE REACTION
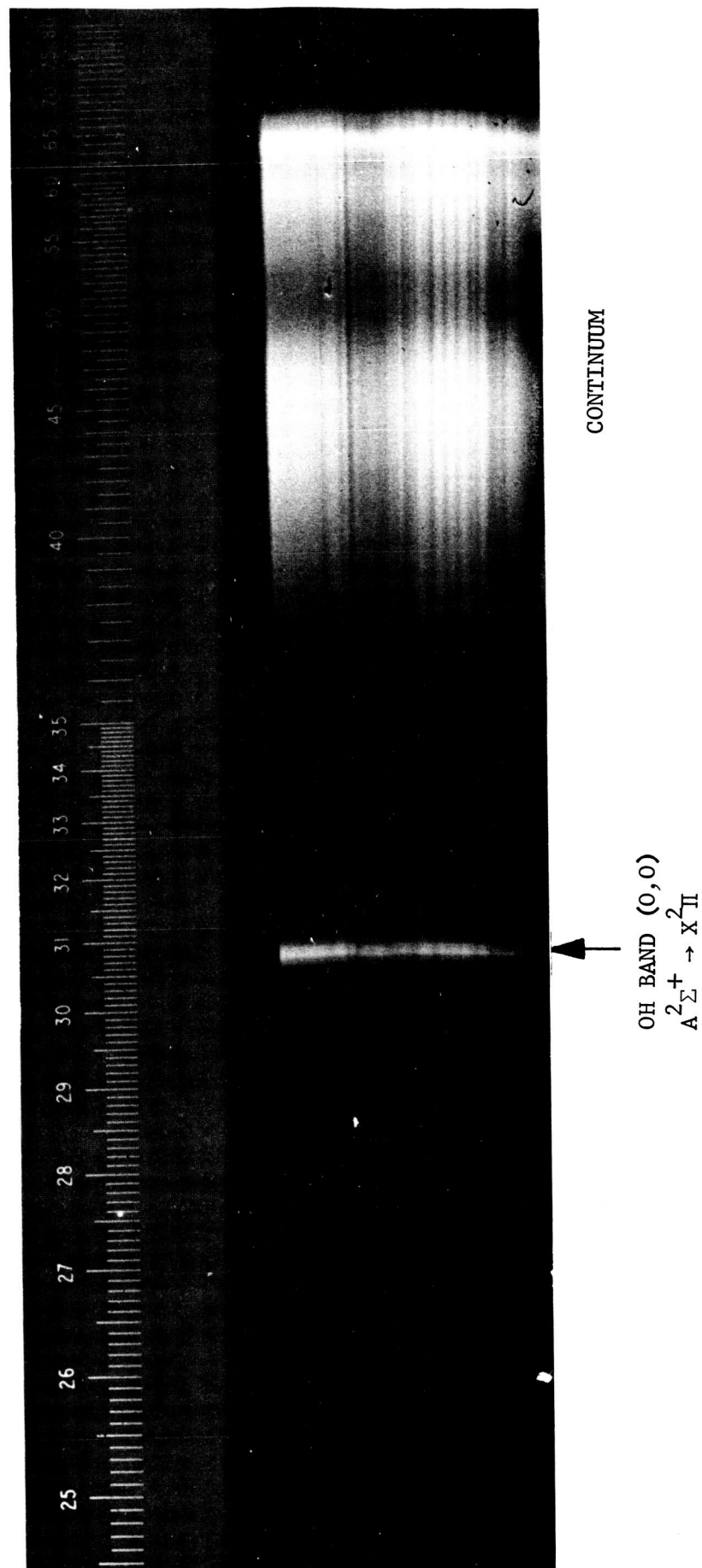OF TRIMETHYL ALUMINUM WITH ATOMIC OXYGEN

PLATE 2 - The spectrum photographed with a small quartz spectrograph.

The intensity of the chemiluminescence produced during the reaction of diethyl zinc and atomic oxygen was low and therefore a good spectrum could not be obtained. However the recorded spectrum shows an apparently continuous emission with two peaks between 4000Å and 4500Å and an OH band at 3100Å. A number of unidentified spectral features are observable in the recorded spectrum from 3000Å to 6000Å. In the spectrum of the diffusion flame of dimethyl zinc, Egerton, et al. [9] have observed a band of ZnO at 3435.32Å which can also be identified in the present spectrum. Since no definite information of the ZnO spectrum is available the study of the chemiluminescent reaction of organo zinc compounds with atomic oxygen should be able to give more information about its spectrum.

The observation of the OH band at about 3100Å in the spectra of the chemiluminescent reactions of organo metallic compounds with atomic oxygen can be compared with the observation of the OH band in the spectra of chemiluminescent reaction between organic compounds [6] and atomic oxygen. This is due to the common organic component in the two types of compounds.

The chemiluminescent reactions between the above mentioned organometallic compounds with atomic oxygen were also observed at 100μ and 30μ pressure. Keeping the oxygen and argon flow constant, the intensity variation of the glow of chemiluminescence produced during the reaction of trimethyl aluminum and atomic oxygen was observed with the flow rate variation of trimethyl aluminum. It was found that with the increase of the flow rate of trimethyl aluminum the intensity of the glow at first, rose very rapidly and then attained a maximum, after which a further increase in the flow rate of trimethyl aluminum slowly quenched the chemiluminescence. After some time, it was found that the inlet tubes were coated with white metallic oxide and the subsequent observations showed decreasing maximum intensity of the chemiluminescence. This is probably due to the rapid recombination of atomic oxygen at the surface coated by metallic oxide. Elias, et al. [19] have shown that silver foil as well as a surface coated with mercuric oxide rapidly recombines the oxygen atom. Linnet [20] has also found a similar effect in the case of other metallic oxides. Due to the rapid contamination of the low pressure system the quantitative information about the chemiluminous efficiencies of different organometallic compounds could not be obtained. However, it was found that the chemiluminescent glow produced during the reaction of atomic oxygen and the above organometallic compounds can be visually observed down to a pressure of about 30μ. Some indication regarding the relative chemiluminous efficiency of the above reactions can be obtained from Figure 8.

CONCLUSIONS

The above observations are insufficient to determine the mechanism for the production of chemiluminescence. However, some general conclusions can be obtained.

It has been earlier postulated by Rosenberg, et al. [18] that the production of chemiluminescence during the night-time release of trimethyl aluminum in the upper atmosphere is due to the recombination of AlO with atomic oxygen, i.e.,

$$AlO + O \rightarrow AlO_2^*$$ (1)

$$AlO_2^* \rightarrow AlO_2 + h\nu \text{ (continuum)}$$
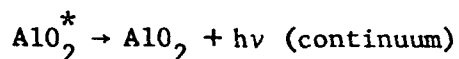
In order to explain the long persistance of night-time glow they have further assumed that the AlO molecules are regenerated by the following reaction,

$$AlO_2 + O \rightarrow AlO + O_2$$ (2)

The observation [18] of AlO bands during the twilight release of trimethyl aluminum in the upper atmosphere supports the above mechanism. It may be noted that the above mechanism is similar to that responsible for the production of chemiluminescence during the reaction of atomic oxygen with nitric oxide. Since the boron belongs to the same group of elements as aluminum, a similar behavior is expected from the reaction between trimethyl boron and atomic oxygen. The observation of BO and BO_2 bands in the spectra of the chemiluminescent reaction between the above organoborane compounds and atomic oxygen supports the above conclusion.

The lack of definite spectroscopic information about ZnO, ZnO_2, and SbO_2 molecules prohibits similar conclusions about the chemiluminous reactions of diethyl zinc and trimethyl antimony. In order to have a clear understanding of the mechanism of the above reactions, the identification and measurements of the intermediate and final products should be undertaken, which may be accomplished by the mass spectrometric analysis of the reaction system.

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